

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
11 August 2005 (11.08.2005)

PCT

(10) International Publication Number  
**WO 2005/073415 A1**

(51) International Patent Classification<sup>7</sup>: **C22B 3/40**, 23/00

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(21) International Application Number:  
PCT/AU2005/000088

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(22) International Filing Date: 28 January 2005 (28.01.2005)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
2004900457 28 January 2004 (28.01.2004) AU  
2004904165 27 July 2004 (27.07.2004) AU  
2004906242 29 October 2004 (29.10.2004) AU

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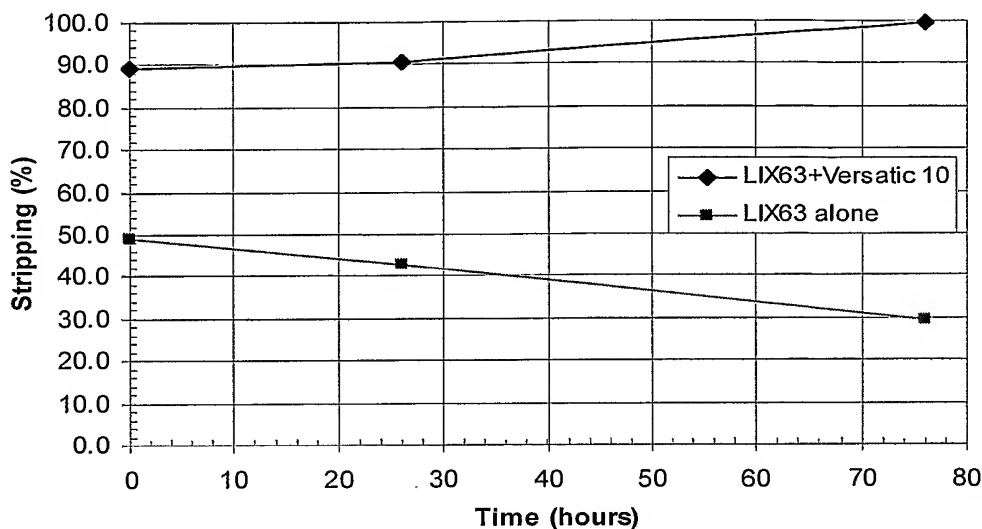
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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[Continued on next page]

(54) Title: SOLVENT EXTRACTION PROCESS FOR SEPARATING COBALT AND/OR MANGANESE FROM IMPURITIES IN LEACH SOLUTIONS



(57) Abstract: A process for the separation of cobalt and/or manganese from impurity elements selected from one or more of calcium and magnesium contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic solution of a carboxylic acid such as Versatic 10 and a hydroxyoxime such as LIX 63, optionally together with a stabilizer.

WO 2005/073415 A1



**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

- 1 -

SOLVENT EXTRACTION PROCESS FOR SEPARATING COBALT AND/OR  
MANGANESE FROM IMPURITIES IN LEACH SOLUTIONS.

5 The present invention relates to a process for separating  
cobalt and/or manganese from calcium and magnesium  
contained in an aqueous solution such as an aqueous leach  
solution, and for recovering the cobalt and/or manganese  
where desired.

10 The world mineral industry is experiencing an  
unprecedented interest in metal extraction from laterite  
and sulphide ores through hydrometallurgical processes.  
Commonly, the hydrometallurgical process involves  
grinding, leaching and solvent extraction (SX), with  
15 recovery of product via precipitation or reduction  
processes. The intensity of the leaching process  
(temperature, pressure, bio) depends on the nature of the  
ore (mineralogy, grade), the distribution of the metal(s)  
to be recovered and the particle size reduction achieved  
20 during grinding. Leach solutions often contain copper,  
nickel, cobalt and zinc (and/or manganese) as metals to be  
recovered (target metals), with calcium, magnesium, iron  
and aluminium (and manganese if not to be recovered) as  
impurity metals to be rejected. Iron (as ferric) and  
25 aluminium are often removed by precipitation at low pH (pH  
2.5 - 5.0) prior to SX.

Separations of industrial significance that have proven to  
be particularly troublesome include:

- 30 - the separation of cobalt (and optionally nickel) from  
manganese (and calcium and magnesium), where  
manganese is to be rejected, and  
- the separation of manganese (and cobalt and nickel)  
from calcium and magnesium, where manganese is to be  
35 recovered.

Traditionally, sulphide or hydroxide precipitation followed by re-leach processes have been used by industry to effect these separations.

5 Drawbacks of sulphide precipitation include:

- The separation of manganese from cobalt by sulphide precipitation is incomplete and causes problems in the downstream processes.
- The re-leaching of sulphides needs high temperature and  
10 pressure, indicating high capital and operating costs.
- The separation of copper and zinc from nickel and cobalt needs separate processes.

15 The drawbacks of the hydroxide precipitation process include:

- The use of magnesia as precipitation agent (if used to prevent gypsum formation) adds cost to the operation.
- Manganese is partially precipitated.
- The use of ammoniacal leaching (if used) to separate  
20 cobalt from manganese results in complexity of the flowsheet and causes serious problems in the downstream processes.
- Ammonia is expensive and the scrubbing and recovery of ammonia are difficult.
- 25 • The separation of copper and zinc from nickel and cobalt needs separate processes.

It is an object of the invention to provide alternative processes for:

- 30 - Separating cobalt from calcium and magnesium, and optionally manganese, especially for solutions deficient in nickel, and
- Separating manganese from calcium and magnesium, especially for solutions deficient in cobalt and  
35 nickel.

Summary of the Invention

The present invention is generally based on the development of an organic solution of a carboxylic acid and a hydroxyoxime which is effective in shifting the pH isotherms of nickel, cobalt, copper, zinc, magnesium, manganese and calcium in such a way as to enable separation of certain groups of these elements from each other. In particular, the isotherms of the elements copper, zinc, nickel and cobalt are separated from the isotherm of manganese to allow effective separation of manganese from these elements. Further, the isotherm of manganese is sufficiently separated from the isotherms of calcium and magnesium to allow effective separation of manganese from calcium and magnesium. Thus, when used in combination with certain leach solutions containing appropriate levels of elements, and in appropriate pH conditions, it becomes possible to separate (and optionally thereafter recover) cobalt and/or manganese from (manganese) calcium and magnesium. Under some conditions, the organic solution of carboxylic acid and hydroxyoxime may be susceptible to degradation, particularly with respect to the hydroxyoxime component. Accordingly, a stabilizer may advantageously be added.

According to the present invention there is provided a process for the separation of cobalt and/or manganese from impurity elements selected from one or more of calcium and magnesium contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic solution of a carboxylic acid and a hydroxyoxime. In some situations there is a need to separate cobalt from manganese only and therefore there is also provided a process for the separation of cobalt from manganese contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic

- 4 -

solution of a carboxylic acid and a hydroxyoxime. The organic solution may optionally further comprise a stabilizer.

5 The present invention is a particular example of a more general process for separating one or more of nickel, cobalt and manganese from the impurity elements (manganese) calcium and magnesium contained in a leach solution, which process comprises the steps of subjecting  
10 the leach solution to solvent extraction using a carboxylic acid and a hydroxyoxime. The process of the invention that is the subject of this application is particularly suited to leach solutions containing low levels of nickel, since nickel has slow extraction and  
15 stripping kinetics in the absence of further additives.

The solvent extraction step described above achieves very good separation of cobalt (and/or manganese) present in the leach solution from (manganese,) calcium, magnesium  
20 and chloride impurity elements which may be present, and good separation of cobalt from manganese if cobalt is to be recovered and manganese is to be rejected as an impurity element. If zinc and copper are present, the process comprises separation of zinc, copper, cobalt  
25 (and/or manganese) from impurity elements selected from one or more of calcium, magnesium (and manganese) contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic solution comprising a  
30 carboxylic acid and a hydroxyoxime. According to a preferred embodiment, the organic solution further comprises a stabilizer.

According to one embodiment, the elements cobalt and/or  
35 manganese extracted into the organic phase during solvent extraction are recovered therefrom. Where the organic phase of the extraction step contains primarily cobalt or

manganese alone, the recovery step may comprise bulk stripping of the element from the organic phase. The bulk stripping may optionally be combined with ion exchange to remove any minor amounts of impurity elements, such as zinc, copper and nickel to improve the purity of the recovered elements. Another optional process for improving the purity of the recovered element is sulphide precipitation. Sulphide precipitation is more suited to precipitation of any minor amounts of copper, zinc, cobalt and nickel present in the manganese recovered from stripping.

In the situation where the leach solution contains both cobalt and manganese, and these are both extracted into the organic phase, the recovery step may comprise selective stripping of the organic phase to separate the manganese from the cobalt. The manganese may thereafter be recovered from the loaded strip liquor, and the cobalt recovered from the selectively stripped organic solution by bulk stripping.

#### Brief Description of the Drawings

The invention will be described in further detail with reference to the following figures which relate to preferred embodiments of the invention.

Figures 1 and 2 are graphs comparing extraction pH isotherms of metals using a comparative extraction system (Figure 1) and the extraction system of one embodiment of the invention (Figure 2).

Figure 3 is a graph showing the extraction kinetics of metals from a leach solution using the extraction system of one embodiment of the invention.

- 6 -

Figure 4 is a graph showing the stripping kinetics of metals from a loaded organic phase from the extraction system of one embodiment of the invention.

5 Figure 5 is a graph comparing stripping kinetics of cobalt using a comparative extraction system and the extraction system of one embodiment of the invention.

10 Figures 6 and 7 are graphs comparing extraction pH isotherms of metals using a comparative extraction system (Figure 6) and the extraction system of one embodiment of the invention (Figure 7).

15 Figure 8 is a graph showing the extraction kinetics of manganese from a leach solution using the extraction system of one embodiment of the invention.

20 Figure 9 is a graph showing the stripping kinetics of manganese from a loaded organic phase from the extraction system of a one embodiment of the invention.

Figure 10 a schematic flow chart of the steps of the process of one embodiment of the invention.

25 Figure 11 is a schematic flow chart of the steps of the process of a second embodiment of the invention.

Figure 12 is a schematic flow chart of the steps of the process of a third embodiment of the invention.

30 Figure 13 is a schematic flow chart of the steps of the process of a fourth embodiment of the invention.

#### Detailed Description of the Invention

35 At the core of the present invention is a synergistic solvent extraction step which effects extraction of a



large proportion of the nickel, cobalt, copper, and zinc into an organic phase (to the extent that these elements are present), with a large proportion of the calcium, magnesium, and chloride being rejected to the aqueous phase. Depending on the pH selected, the manganese can report to either the organic phase or the aqueous phase, as is chosen for a particular leach solution. The solvent extraction is conducted with a combination of carboxylic acid and a hydroxyoxime synergist, and optionally a stabilizer.

The hydroxyoxime synergist is capable of increasing the pH gap,  $\Delta\text{pH}_{50}$ , between isotherms for nickel and cobalt and that for manganese, and between the isotherm for manganese and those for calcium and magnesium. This results in advantageous selectivity of nickel and cobalt and optionally manganese, over the impurities (manganese), calcium, magnesium and chloride.

The  $\text{pH}_{50}$  value is the pH at which 50% metal extraction is achieved. Thus,  $\Delta\text{pH}_{50}$  is the difference between the  $\text{pH}_{50}$  values for two metals, or the difference between the  $\text{pH}_{50}$  values for the same metal under different extraction conditions.

#### Carboxylic acid

In the most preferred embodiment of the invention, the carboxylic acid is 2-methyl, 2-ethyl heptanoic acid (commercially available as Versatic 10) or a cationic exchange extractant having extraction characteristics similar to 2-methyl, 2-ethyl heptanoic acid could be used. Cationic exchange extractants have hydrogen ions which are exchanged with metal ions in the aqueous solution. The term carboxylic acid is used in its broadest sense to refer to any organic carboxylic acid. Carboxylic acids have the formula  $\text{RCOOH}$ , in which R represents any optionally substituted aliphatic or aromatic group, or

combinations of these groups, including optionally substituted alkyl, alkenyl, alkynyl, aryl, or heteroaryl groups (and combinations thereof). Preferably R represents a relatively bulky group containing at least 4 carbon atoms, and preferably between 4 to 18 carbon atoms.

The term "alkyl" used either alone or in a compound word such as "optionally substituted alkyl" or "optionally substituted cycloalkyl" denotes straight chain branched or mono- or poly-cyclic alkyl, preferably C1-30 alkyl or cycloalkyl, most preferably C4-18 alkyl. Examples of straight chain and branched alkyl include methyl, ethyl, butyl, isobutyl, tert-butyl, 1,2-dimethylpropyl, 1-methylpentyl, 5-methylhexyl, 4,4-dimethylpentyl 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,1,2-trimethylbutyl, nonyl, 1- 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 2-hexyl 2-methyloctyl and the like. Examples of cyclic alkyl include cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclodecyl and the like. The alkyl may optionally be substituted by any non-deleterious substituent.

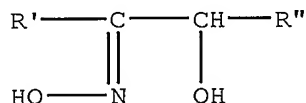
In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl,

alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthiom benzylthio, acylthio and the like.

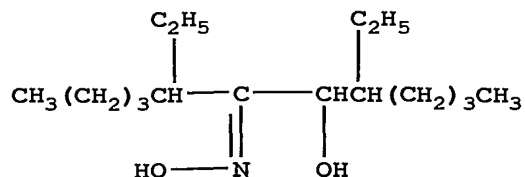
Suitable optional substituents will be chosen on the basis that the carboxylic acid have the desired extraction characteristics, and the substituents do not react with any other component of the mixture under the given extraction conditions.

#### 10 Hydroxyoxime

A hydroxyoxime is used as a synergist with the carboxylic acid in the solvent extraction step. A hydroxyoxime is a compound containing an oxime group and a hydroxy group. Preferably, the groups are in an  $\alpha$ -position with respect to each other. Such  $\alpha$ -hydroxyoximes are chelating, whereas oximes are generally non-chelating and thus behave differently. The "oxime" functional group contains a carbon to nitrogen double bond, with the nitrogen atom being attached to an oxygen atom. Accordingly, the term oxime includes within its scope oximes with a hydroxy group attached to the nitrogen atom, and oxime ethers, although hydroxime ( $>C=N-OH$ ) is preferred. The hydroxyoxime may be a C8-C26 hydroxyoxime. Preferably, the hydroxyoxime is an aliphatic hydroxyoxime. Preferably, the hydroxyoxime is of the formula:



in which R' and R'' are each selected from an optionally substituted, straight chain, branched or cyclic alkyl, group containing from 2 to 12 carbon atoms. Preferably each of R' and R'' are unsubstituted alkyl groups, most preferably a heptyl group. An example of such a compound is 5,8-diethyl-7-hydroxy-6-dodecanone oxime (the active component of a commercial agent LIX 63). This has the following structure:



### Stabilizer

5 Under some conditions, the reagent mixture of carboxylic acid and hydroxyoxime may be susceptible to degradation, particularly with respect to the hydroxyoxime component. Accordingly, a suitable stabilizer may advantageously be used to slow any degradation reaction. Degradation may

10 take place via a number of mechanisms, including oxidation and hydrolysis. Hence the stabilizer is suitably one that mitigates against oxidation and/or hydrolysis of the hydroxyoxime. Such stabilisers include, but are not limited to, esters (e.g. TXIB), ethers, ketones, alcohols (e.g.

15 isodecanol, TDA) and alkylphenols (e.g. nonylphenol, dodecylphenol, BHT, Ionol). Preferably the stabilizer is an anti-oxidant. Of these, we have found the alkylphenol anti-oxidants to be particular useful. The term

20 "alkylphenol" encompasses all alkyl derivatives of phenol, and in particular those derivatives with one or more straight chain, branched or cyclic alkyl substituents. The alkylphenol 2,6-bis(1,1-dimethylethyl)-4-methyl phenol (commercially available as BHT and Ionol) or reagents with similar anti-oxidant characteristics to 2,6-bis(1,1-

25 dimethylethyl)-4-methyl phenol are particularly useful.

### Leach solution

The leach solution subjected to the synergistic solvent extraction with the organic solution of carboxylic acid,

30 hydroxyoxime and optionally a stabilizer may be any type of leach solution containing cobalt and/or manganese, together with impurity elements selected from one or more of calcium, magnesium, (manganese) and chloride,

- 11 -

optionally together with copper and zinc. Preferably, the leach solution is one containing little nickel.

5 In this respect, the leach solution suitably contains less than 100ppm nickel, or any other low level that does not warrant recovery for economic reasons. Where cobalt is to be recovered, the nickel is suitably present in any amount of less than 50% of that of cobalt (for example, <100ppm nickel, >200ppm cobalt).

10

According to one embodiment, the leach solution may contain the following levels of elements:

Ni: 0 - 100 ppm  
15 Co: 100 ppm - 5 g/L  
Cu: 0 - 100 ppm  
Zn: 0.2 - 2 g/L  
Ca: 1ppm - saturated, for instance between 0.5 - 0.7 g/L  
Mn: 0.2 - 50 g/L, or 1-50 g/L  
20 Mg: 1ppm - 100 g/L, or 2-100 g/L.

The leach solution may for instance be a pregnant leach solution obtained from the pressure acid leaching of any suitable ore type, such as a laterite or sulphide ore. It  
25 may alternatively be a solution from bio-leach, atmospheric acid leach, oxidative leach, reductive leach, chloride leach or any combination of these leach processes. The steps involved in producing such leach solutions are well known in the art.

30

The leach solution is preferably a solution that has been subjected to a preliminary iron and/or aluminium precipitation step to precipitate out iron and/or aluminium to leave an aqueous leach solution containing  
35 the target elements and impurity elements identified above. The leach solution may alternatively or further

have been subjected to one or more additional treatment or processing stages.

Synergistic solvent extraction conditions

5 The solvent extraction step involves contacting an organic solvent containing the carboxylic acid, hydroxyoxime and optionally stabilizer with the (aqueous) leach solution. The organic solvent may be any suitable organic solvent known in the art. Kerosene is the most common  
10 solvent/diluent used for this purpose due to its low cost and availability. Shellsol 2046 is one specific example.

The amount of carboxylic acid and hydroxyoxime (and stabilizer) in the organic solution used in the solvent  
15 extraction step will depend on the concentration of the (nickel), cobalt (and optionally manganese) or both to be extracted and the A/O (aqueous/organic) flow rate ratio. The concentration would typically be in the range of from 0.1 to 2.0 M for carboxylic acid, with a preferred range  
20 of 0.1 to 1.0M, and 0.05 to 1.0 M for hydroxyoxime. The concentration of stabilizer may be in the range of from 0 to 0.1 M, typically 0.005 to 0.1 M.

Preferably, the pH of the aqueous phase is maintained in a  
25 range from 3.5 to 5.0 and more preferably 4.0 to 4.5 in the extraction step if manganese is to be rejected. Preferably, the pH of the aqueous phase is maintained in a range from 5.5 to 7.0 and more preferably 5.8 to 6.3 in the extraction step if manganese is to be recovered. The  
30 temperature is preferably maintained in the range of from 10°C to 60°C, more preferably from 20 to 40°C. Whilst temperatures as low as 10°C are achievable, a temperature lower than 15°C results in high viscosity. At temperatures higher than 60°C there is a risk of increased evaporation  
35 and degradation of the organic phase.

The aqueous to organic ratio (A/O) in the extraction step

- 13 -

is most suitably 1:1, but may lie in the range from 10:1 to 1:10, and preferably 1:5 to 5:1. The aqueous to organic ratio maintained in the scrubbing step may lie within the range from 1:5 to 1:200, but preferably it is in the range of 1:5 to 1:20.

The cobalt and/or manganese extracted into the loaded organic phase in the synergistic solvent extraction can be recovered in downstream processing stages.

#### Scrubbing

The organic phase from the synergistic extraction step of the invention is suitably subjected to scrubbing. The scrub solution may suitably be a process stream recycled from the process, and is preferably derived from an aqueous stream of a stripping stage (which may be a selective stripping stage) following the scrubbing stage.

#### Recovery of cobalt, manganese or both from scrubbed organic solution

There are a number of options envisaged by the applicants for the recovery of cobalt, manganese or both from the scrubbed organic solution. One example for the situation where both cobalt and manganese are extracted (i.e. pH of aqueous phase in extraction is 5.5 to 7.0) is set out below. It is noted that other options within the skill and knowledge of those in the art could be used in place of the following, and are within the scope of the present invention. Moreover, different steps would be used for different leach solutions containing different levels of elements, or when other elements are desired to be recovered or removed.

#### Selective stripping to separate cobalt and manganese

According to one embodiment of the invention, the organic phase containing cobalt and manganese is subjected to selective stripping to separate to a significant extent

the cobalt and the manganese. The selective strip suitably involves contacting the organic phase from the synergistic extraction with an acidic aqueous solution to yield (a) a loaded strip liquor containing manganese and  
5 (b) a selectively stripped organic solution containing cobalt (and zinc, nickel and copper, if they were present in the organic phase from the synergistic extraction).

The acidic aqueous solution for the selective strip is  
10 suitably sulphuric acid solution, although other aqueous acid solutions known in the art (such as hydrochloric) may be used. The pH of the acidic aqueous solution is suitably in the range of about 4.0 to 5.0, depending on the level of separation desired. Most preferably, the pH  
15 is about 4.5.

The combination of the described synergistic extraction with the selective strip of manganese from cobalt is a very useful combination, enabling the recovery of  
20 manganese and cobalt using only one solvent extraction circuit (although more than one circuit could be used if so desired with other process steps).

#### Other process details

25 The synergistic extraction step of the present invention may be combined with different preliminary and following process steps for the development of processes suitable for the recovery of cobalt and/or nickel when different  
30 impurity elements may be present.

It will be well understood to persons skilled in the art of the invention that scrubbing stages of the type well known in the art may be used for recovering elements even  
35 if the scrubbing stages are not specifically mentioned. The design of the optimum arrangement of scrubbing stages will depend on the specific aqueous leach solution and the



- 15 -

elements desired to be recovered therefrom (and target percentage recovery levels).

It is also an advantage of the present invention that cobalt can be separated from impurities contained in leach solutions without intermediate precipitation of the cobalt with other impurity elements and re-leaching of the precipitate to subsequently enable the removal of the impurities. Thus, in a preferred embodiment of the invention, the process does not include a precipitation step involving precipitation out of the target elements and re-leaching of the precipitate.

#### Examples

The present invention will now be described in further detail with reference to the following examples which demonstrate the underlying theory behind the invention, and how the invention is put into practice.

#### *Batch Test Work*

Example 1 - Extraction pH isotherms of metals with Versatic 10 / LIX63 synergistic system.

This example illustrates that when carboxylic acid Versatic 10 is used as the extractant with no added synergist, the pH isotherms of the "valuable" elements Zn, Ni, and Co are too close to the isotherms of the "impurity" elements Mn, Ca and Mg for effective separation. However when a synergistic system comprising Versatic 10 and hydroxyoxime LIX 63 is used, the isotherms of the "valuable" elements Cu, Zn, Ni, and Co are sufficiently separated from the isotherm of Mn to allow effective separation. Further, the isotherm of Mn is sufficiently separated from the isotherms of Ca and Mg to allow effective separation.

The aqueous solution was a synthetic solution to simulate

- 16 -

a typical laterite leach solution containing 3 g/L Ni, 0.3 g/L Co, 0.2 g/L Cu and Zn, 2 g/L Mn, 10 g/L Mg and 0.5 g/L Ca.

5 The metal extraction pH isotherms with the 0.5 M Versatic 10 (carboxylic acid) alone were determined and plotted, as shown in Fig. 1. The metal extraction pH isotherms using the combination of 0.5 M Versatic 10 and 0.35 M LIX63 (hydroxyoxime) were also determined and plotted in Figure 10 2. Comparison of the two figures reveals that the combination of LIX63 with Versatic 10 resulted in significant synergistic extraction isotherm shifts (to lower pH) for nickel, cobalt, copper, zinc, and manganese and antagonistic shifts (to higher pH) for calcium and 15 magnesium. As shown in Figure 2, with the 0.5 M Versatic 10 / 0.35 LIX63 system, the  $\Delta\text{pH}_{50}$  values of nickel, cobalt, copper, zinc, manganese and Ca were found to be 2.8, 3.5, >2.0, 2.0, 1.2 and -0.5 pH units, respectively.

20  $\text{pH}_{50}$  of metals from pH isotherms in Figs 1 and 2

Metal	$\text{pH}_{50}$		$\Delta\text{pH}_{50}$
	0.5M Versatic 10	0.5M Versatic 10 + 0.35M LIX 63	
Ni	6.2	3.4	2.8
Co	6.3	2.8	3.5
Cu	4.1	<2.0	>2.0
Zn	5.7	3.7	2.0
Mn	6.5	5.3	1.2
Ca	7.0	7.5	-0.5

The  $\Delta\text{pH}_{50}(\text{Mn-Ni})$  value for the 0.5 M Versatic 10 / 0.35 M LIX63 system was found to be 1.9 pH units and the  $\Delta\text{pH}_{50}(\text{Mn-Co})$  value 2.5 pH units, indicating easy separation of 25 nickel and cobalt from manganese, calcium and magnesium. The  $\Delta\text{pH}_{50}(\text{Ca-Mn})$  value for the 0.5 M Versatic 10 / 0.35 M LIX63 system was found to be 2.2 pH units, indicating easy separation of manganese from calcium and magnesium.

30 Example 2 - Extraction kinetics with Versatic 10 / LIX63

- 17 -

synergistic system.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Cu, Co, Zn and Mn display fast extraction kinetics, while the extraction kinetics for Ni are slow. Hence this system is potentially suitable for Cu, Co, Zn and Mn recovery when the leach solution contains little Ni.

Tests were conducted to establish the extraction kinetics of the metals in the synthetic laterite solution using Versatic 10/LIX63. The extraction kinetics of copper, cobalt, zinc (and manganese - see Example 6 and Fig 8) were found to be fast and the extraction kinetics of nickel were found to be relatively slow (Fig. 3). Within 30 seconds, only 55% Ni was extracted and within 2 minutes, only 74%. It is noted that Mn and Zn are crowded out as Ni extracts.

Example 3 - Stripping kinetics with Versatic 10 / LIX63 synergistic system.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Cu, Co, Zn and Mn display fast stripping kinetics, while the stripping kinetics for Ni are slow. Hence this system is potentially suitable for Cu, Co, Zn and Mn recovery when the leach solution contains little Ni.

Tests were conducted to determine the stripping kinetics of the metals from the 0.5 M Versatic 10 / 0.35 M LIX63 system using a strip solution containing 5 g/L Ni and 10 g/L sulphuric acid (Fig. 4). The stripping kinetics of copper, cobalt and zinc were fast. The stripping kinetics of nickel were slow, with only 18% of the nickel being stripped after 2 minutes of mixing.

- 18 -

Example 4 - Stripping of cobalt from LIX63 alone and Versatic 10 / LIX63 systems.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Co displays fast stripping kinetics, however when LIX 63 alone is used, Co cannot be readily stripped thus making LIX 63 alone an unsuitable extractant for Co-containing solutions.

Cobalt(II) can poison hydroxyoxime reagents such as LIX63. This means that once cobalt(II) is extracted by hydroxyoxime reagents (and oxidises to Co(III)), it cannot be stripped with concentrated acids. Tests were conducted to see whether the new system results in cobalt poisoning of the extractant/synergist.

Parallel tests were conducted with 0.35 M LIX63 alone and 0.5 M Versatic 10 / 0.35 M LIX63 systems by mixing the organic solutions with aqueous solution containing cobalt (Fig. 5). The organic and aqueous solutions were left in contact with air bubbling for 76 hours. Thereafter, a sulphuric acid solution of 100 g/l sulphuric acid was used to strip cobalt from the loaded organic solution sample. The cobalt stripping efficiency from the 0.35 M LIX63 alone system was only 29.2% after 10 minutes stripping. The cobalt stripping efficiency for the 0.5 M Versatic 10 / 0.35 M LIX63 system was 99.5%. This indicates that cobalt(II) does not poison the Versatic 10 / LIX63 system.

Example 5 - Extraction pH isotherms of metals with Versatic 10 / LIX63 system.

This example illustrates that when Versatic 10 is used as the extractant with no added synergist, the pH isotherm of Mn is too close to the isotherms of the "impurity elements" Ca and Mg for effective separation. However

when the synergistic system comprising Versatic 10 and LIX 63 is used, the isotherm of Mn is sufficiently separated from the isotherms of Ca and Mg to allow effective separation.

5

The aqueous solution was a synthetic solution to simulate a typical waste laterite leach solution containing 1.46 g/L Mn, 17.6 g/L Mg and 0.54 g/L Ca.

10 The extraction pH isotherms were determined for 0.5 M Versatic 10 alone and 0.5 M Versatic 10 / 0.2 M LIX63 systems and shown in Figs. 6 and 7, respectively. The  $\text{pH}_{50(\text{Mn})}$  decreased from 6.9 to 5.6 pH units while the positions of isotherms of magnesium and calcium remained  
15 virtually unchanged. At pH 6.5, the extractions of manganese, calcium and magnesium were 17.9%, 2.84% (or 46 ppm) and 0.16% (or 82 ppm), respectively, for the Versatic 10 alone system while the extractions of manganese, calcium and magnesium were 87.3%, 2.41% (or 39 ppm) and  
20 0.05% (or 26 ppm), respectively, for the Versatic / LIX63 system. This indicates that the selectivity of Versatic 10 for manganese over magnesium and calcium was very greatly improved.

25 Example 6 - Extraction kinetics with Versatic 10 / LIX63 system.

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Mn displays  
30 fast extraction kinetics. Hence this system is suitable for Mn recovery.

The extraction kinetics of the metals in the synthetic waste laterite leach solution using the 0.5 M Versatic 10  
35 / 0.2 M LIX63 system were determined and graphed in Fig. 8. As shown, the extraction kinetics of manganese were fast. Within 0.5 minutes, the system almost reached

equilibrium with manganese extraction of 80%.

Example 7 - Stripping kinetics with Versatic 10 / LIX63 system.

5

This example illustrates that when the synergistic system comprising Versatic 10 and LIX 63 is used, Mn displays fast stripping kinetics. Hence this system is suitable for Mn recovery.

10

The stripping kinetics of the manganese in the loaded 0.5 M Versatic 10 / 0.2 M LIX63 system were determined using a strip solution containing 60 g/L Mn and 35 g/L sulphuric acid and graphed in Fig. 9. As shown, the stripping kinetics of manganese were fast. Within 0.5 minutes, the system almost reached equilibrium with manganese extraction of 99%.

15

*Process Flowcharts*

20

Example 8 - Process for separation and recovery of cobalt and manganese from leach solutions.

Based on the above findings, a new direct solvent extraction (DSX) process flow sheet was designed. The flow sheet is shown in Figure 10.

25

*Leach solution*

The leach solution contains manganese and cobalt, as well as the impurity elements calcium and magnesium, but little or no copper, zinc or nickel. A suitable solution composition for this flow sheet may comprise Co > 200 ppm, Mn > 1 g/L, Ca < 50 g/L (Ca will be < 1 g/L in sulphate solutions), Mg < 100 g/L, Cu, Zn and Ni < 100 ppm (or of no economic value). It is noted that the flow sheet is not limited to such leach solutions, and the leach solutions may comprise different levels of the given elements, optionally together with further impurity

35

- 21 -

elements. This leach solution is one that may have been subjected to preliminary neutralisation with limestone at pH 4.5 - 5.0 to precipitate impurity elements Fe (III), Al, Si and Cr.

5

#### Synergist solvent extraction (SSX EX)

In the synergistic solvent extraction step, an organic solution of carboxylic acid (Versatic 10), a hydroxyoxime (LIX 63) and a stabilizer (Ionol) in organic diluent Shellsol 2046 is contacted with the leach solution at pH 6 - 6.5 to obtain (a) an aqueous raffinate containing magnesium and calcium, and (b) a loaded organic solution containing almost all of the cobalt and manganese, and only minor levels of calcium and magnesium.

15

#### Scrubbing (SSX SC)

The organic solution from the extraction step is subjected to scrubbing at pH 5.5 - 6 using a sulphate solution containing a small amount of manganese from the next step of stripping 1, resulting in (a) a scrubbed organic solution containing cobalt and manganese, and (b) a scrub liquor which is recycled to the synergistic solvent extraction step.

#### 25 Selective stripping (SSX ST1)

The scrubbed organic solution is subjected to stripping 1 (selective strip) using a sulphuric acid solution at pH between 4.0 - 5.0 resulting in (a) a loaded strip liquor containing manganese, and (b) a stripped organic solution containing mainly cobalt and only a very small amount of manganese.

The loaded strip liquor is sent to manganese recovery, with one stream returning to the previous scrubbing stage.

35

#### Scrubbing (SSX SC2)

The organic solution from stripping 1 is subjected to scrubbing 2 at a pH of 3.5 - 4.0 using the aqueous strip liquor from a subsequent stripping stage (stripping 2). This step results in (a) a scrubbed organic solution  
5 containing cobalt, and (b) a scrub liquor which is recycled to the original synergistic solvent extraction stage to maximize cobalt recovery.

#### Stripping (SSX ST2)

10 The scrubbed organic solution is subjected to stripping 2 using sulphuric acid solution at pH between 2.0 - 2.5. The cobalt recovered in this stripping stage is optionally subjected to zinc/copper/nickel ion exchange to enable removal of any zinc, copper and nickel impurities present.  
15 The zinc, copper and nickel is disposed of, and the cobalt is sent to cobalt recovery by any process known in the art. One example is cobalt precipitation using base or sulphide.

20 Example 9 - Process for separation and recovery of cobalt from leach solutions.

An alternative solvent extraction process flow sheet was formulated for the recovery of cobalt from leach solutions  
25 containing impurity elements manganese, calcium and magnesium, with little or no copper, zinc or nickel. This flow sheet is shown in Figure 11. A typical solution composition for which this flow sheet could be applicable comprises Co > 200 ppm, Mn < 100 g/L, Ca < 100 g/L (Ca  
30 will be < 1 g/L in sulphate solutions), Mg < 100 g/L, Cu, Zn and Ni < 100 ppm (or of no economic value). Of course, variations in this solution composition are possible.

The plant leach solution (PLS) is adjusted to a pH between  
35 4.0 - 5.0 and subjected to the synergistic solvent extraction (SSX) described in relation to Example 8 above. The organic phase contains the cobalt (as well as zinc,



copper and nickel to the extent that these are present) and a minor level of manganese. The aqueous raffinate contains magnesium, calcium and manganese.

5 Scrubbing is conducted as described above in relation to Example 8, at pH 3.5 - 4.5, yielding (a) a scrubbed organic solution containing principally cobalt, but also zinc, copper, and nickel in very low quantities if present at all in the plant leach solution, and (b) a scrub liquor  
10 which is recycled to the original synergistic solvent extraction stage to maximize cobalt recovery. The organic phase of the scrubbing step contains cobalt, and possibly zinc, nickel and copper, which is then subjected to stripping with sulphuric acid at pH between  
15 2.0 and 2.5. The loaded strip liquor is sent to cobalt recovery (with one stream returning to the previous scrubbing stage), optionally via ion exchange, with the organic phase returned to the synergistic solvent extraction.

20

Example 10 - Process for Separation and Recovery of Cobalt, Copper and Zinc.

Figure 12 details a process flow sheet which is a  
25 variation on that illustrated in Figure 11, and described in Example 9 above.

The process of Figure 12 is suitable for recovering copper, cobalt and zinc from leach solutions that contain  
30 impurity elements manganese, calcium and magnesium, with little or no nickel. A solution composition to which this process may suitably be applied contains the following: Cu > 500 ppm, Co > 200 ppm, Zn > 500 ppm, Mn < 100 g/L, Ca < 100 g/L (Ca will be < 1 g/L in sulphate solutions), Mg <  
35 100 g/L and Ni < 100 ppm (or of no economic value). Of course, variations in this solution composition are also envisaged.

The plant leach solution is subjected to copper solvent extraction and copper electrowinning. The leach solution containing reduced levels of copper, and all other elements, is then subjected to iron and aluminium precipitation (Fe/Al PPT) by neutralising the leach solution with limestone to a pH of between 4.0 - 5.0 to precipitate iron and aluminium. The leach solution is then subjected to the synergistic solvent extraction, scrubbing and stripping as described in relation to Example 9 and Figure 11 above. As will be appreciated, any copper and zinc still present reports to the phases to which the cobalt reports.

The aqueous phases collected from scrubbing and stripping contain cobalt, zinc and minor levels of copper, together with any levels of nickel which may be present. The aqueous liquor is subjected to zinc solvent extraction to remove zinc therefrom for recovery. Thereafter, the cobalt (and nickel and copper) containing solution is subjected to nickel and copper ion exchange to enable nickel and copper removal and disposal. Thereafter, the cobalt is recovered.

Example 11 - Process for separation and recovery of manganese from leach solutions.

A new solvent extraction process flow sheet was developed for recovering manganese from leach solutions that contain the impurity elements calcium and magnesium, with little or no copper, zinc, cobalt or nickel. This is set out in Figure 13. A typical solution composition which may be subjected to this process may comprise Mn > 1 g/L; Ca < 50 g/L (Ca will be < 1 g/L in sulphate solutions); Mg < 100 g/L; Cu, Zn, Co and Ni < 100 ppm (or of no economic value). Of course, variations in this solution composition are envisaged.

- 25 -

The leach solution, which may have been subjected to preliminary processing steps, is subjected to synergistic solvent extraction with the Versatic 10 / LIX 63 / Ionol synergistic system, with the aqueous phase adjusted to a pH between 6.0 - 7.0. The aqueous raffinate contains calcium and magnesium, and the organic phase contains manganese, with minor levels of calcium of magnesium. The organic phase is subjected to scrubbing using a scrub solution at pH between 6.0 - 6.5. The scrub solution is a stream of the manganese sulphate solution generated in a subsequent stripping stage. The organic phase from the scrubbing stage containing manganese is sent to stripping, and the aqueous scrub liquor is recycled to the synergistic solvent extraction stage.

Stripping is performed on the organic phase using sulphuric acid at pH between 3.0 - 4.0. The aqueous strip liquor is optionally subjected to sulphide precipitation to remove any copper, zinc, cobalt or nickel impurities present, and the manganese sent to manganese recovery. A stream of the strip liquor is recycled to the scrubbing stage. This process is particularly suited for situations where the manganese value is acceptable, making it desirable to recover the manganese from a leach solution. If the leach solution contains appreciable levels of cobalt, and other elements having pH isotherms similar to cobalt, then the process of Example 8 and Figures 10 would be more suited.

Example 12 - Effect of stabilizer (Ionol) on degradation of hydroxyoxime (LIX63) in Versatic 10 / LIX63 system.

This example shows how addition of an anti-oxidant stabilizer (Ionol) slows the rate of degradation of the hydroxyoxime LIX63 in the Versatic 10 / LIX63 extraction system.

An organic extractant solution (25 mL) containing 0.4M LIX63 and 0.5M Versatic 10 in Shellsol D70 diluant was loaded with a synthetic leach solution (50 mL) containing 0.5 g/L Ca, 9 g/L Na, 24 g/l Mg, 45 g/L Mn, 0.2 g/L Co, 1 g/L Zn and 0.15 g/L Cu, at pH 4.5 and left to stand in a water bath at 25°C. Two further (duplicate) systems, each containing 10 g/L Ionol were prepared and treated similarly. After 18 days, the organic solution was sampled and analysed for LIX63 using gas chromatography. The results are shown in the table below. After 18 days in the Ionol-free system, 5.2 % of the LIX63 had been degraded. After 18 days in the duplicate systems initially containing 10 g/L Ionol, 0.7% and 1.6% of the LIX63 had been degraded.

Table 1 Oxime concentration in the loaded organic solutions as a function of contact time.

	LIX63 (%) relative to initial concentration		
Contact time (days)	Versatic 10 + LIX63	Versatic 10 + LIX63 + Ionol	Versatic 10 + LIX63 + Ionol
0	100.0	100.0	100.0
8	97.0	99.6	99.2
18	94.8	99.3	98.4

It will be understood to persons skilled in the art of the invention that many modifications may be made to the embodiments described without departing from the spirit and scope of the invention.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but

not to preclude the presence or addition of further features in various embodiments of the invention.

## THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the separation of cobalt and/or manganese from impurity elements selected from one or more of calcium and magnesium contained in a leach solution, or for separating cobalt from manganese contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic solution of a carboxylic acid and a hydroxyoxime.
2. The process of claim 1 wherein the organic solution comprises a stabilizer against hydroxyoxime degradation.
3. The process of claim 2, wherein the stabilizer is an antioxidant.
4. The process of claim 2, wherein the stabilizer is an alkylphenol.
5. The process of any one of claims 1 to 4, wherein the leach solution contains little nickel.
6. The process of any one of claims 1 to 5, wherein the leach solution contains cobalt and/or manganese, together with impurity elements selected from one or more of calcium, magnesium, (manganese) and chloride, optionally together with copper and/or zinc.
7. The process of any one of claims 1 to 6 wherein, the leach solution contains the following levels of elements:  
  
Ni: 0 - 100 ppm  
Co: 100 ppm - 5 g/L  
Cu: 0 - 100 ppm  
Zn: 0.2 - 2 g/L  
Ca: 1ppm - saturated  
Mn: 0.2 - 50 g/L

Mg: 1ppm - 100 g/L

8. The process of any one of claims 1 to 7, wherein the leach solution is a solution that has been subjected to a preliminary iron and/or aluminium precipitation step to precipitate out iron and/or aluminium to leave an aqueous leach solution containing the target elements and impurity elements.
9. The process of any one of claims 1 to 8, wherein the carboxylic acid is 2-methyl, 2-ethyl heptanoic acid or a cationic exchange extractant having extraction characteristics similar to 2-methyl, 2-ethyl heptanoic acid.
10. The process of any one of claims 1 to 9, wherein the hydroxyoxime is a chelating  $\alpha$ -hydroxyoxime.
11. The process of any one of claims 1 to 10, wherein the leach solution contains cobalt and manganese, and the pH of the aqueous phase in the solvent extraction step is maintained in the range of from 5.5 to 7.0 to effect extraction of the cobalt and manganese into the organic phase.
12. The process of claim 11, wherein the pH of the aqueous phase in the solvent extraction step is maintained in the range of from 5.8 to 6.3.
13. The process of claim 11 or claim 12, wherein the organic phase containing cobalt and manganese is subjected to selective stripping to separate to a significant extent the cobalt from the manganese.
14. The process of claim 13, wherein the selective stripping comprises contacting the organic phase from the solvent extraction with an acidic aqueous solution to

- 30 -

yield (a) a loaded strip liquor containing manganese and  
(b) a selectively stripped organic solution containing  
cobalt.

5 15. The process of claim 14, wherein the acidic aqueous  
solution used in the selective stripping has a pH in the  
range of 4.0 to 5.0.

10 16. The process of any one of claims 1 to 10, wherein the  
leach solution contains cobalt and manganese, and the pH  
of the aqueous phase in the solvent extraction step is  
maintained in the range of from 3.5 to 5.0 to effect  
extraction of cobalt into the organic phase and rejection  
of manganese to the aqueous phase.

15 17. The process of claim 16, wherein the cobalt is  
recovered from the organic phase by bulk stripping.

20 18. The process of any one of claims 1 to 17, wherein the  
leach solution comprises zinc and/or copper, the zinc  
and/or copper are extracted into the organic phase with  
the cobalt in the solvent extraction step, and the zinc  
and/or copper are separated from the cobalt by ion  
exchange.

25 19. The process of any one of claims 1 to 10, wherein the  
leach solution comprises manganese and a low level or no  
cobalt, and the manganese is extracted into the organic  
phase to effect separation of manganese from the impurity  
30 elements calcium and/or magnesium.

20. The process of any one of claims 1 to 19, wherein  
scrubbing is conducted on the organic phase after each  
solvent extraction.

35 21. A process for the separation of zinc, copper and  
cobalt from impurity elements selected from one or more of



manganese, calcium and magnesium contained in a leach solution, the process comprising the step of subjecting the leach solution to solvent extraction using an organic solution of a carboxylic acid and a hydroxyoxime.

5

22. The process of claim 21, wherein the organic solution further comprises a stabilizer against hydroxyoxime degradation.

10

23. A product recovered by the process according to any one of claims 1 to 22.

1/9

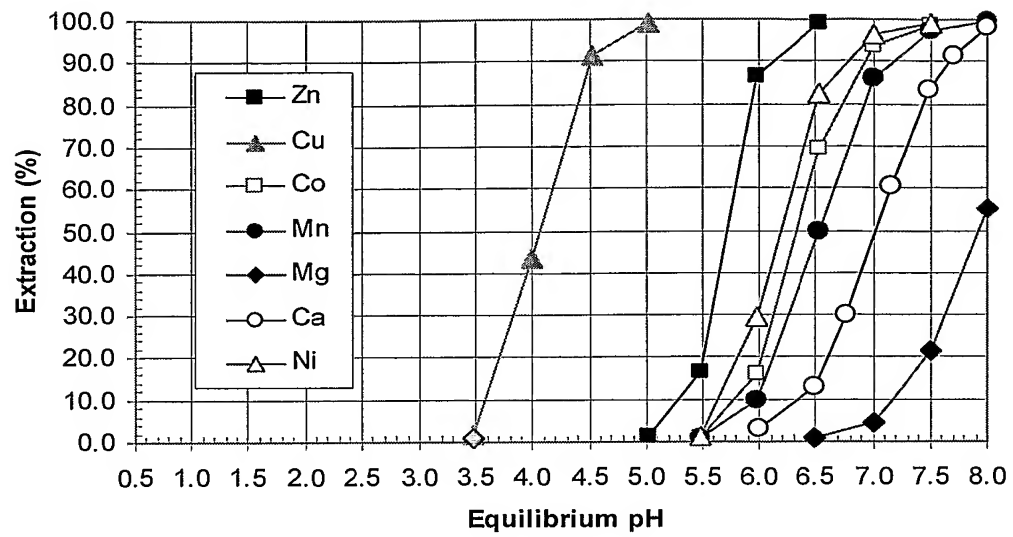


Figure 1

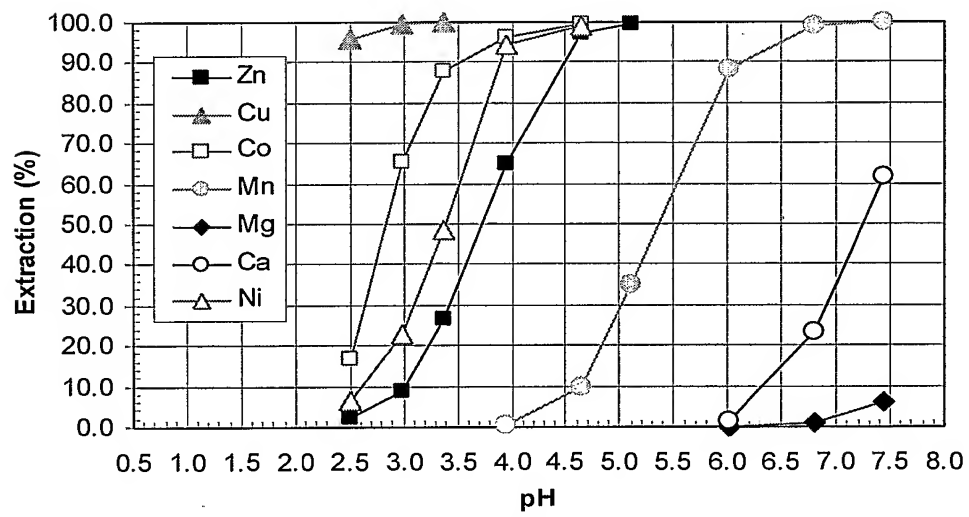


Figure 2

2/9

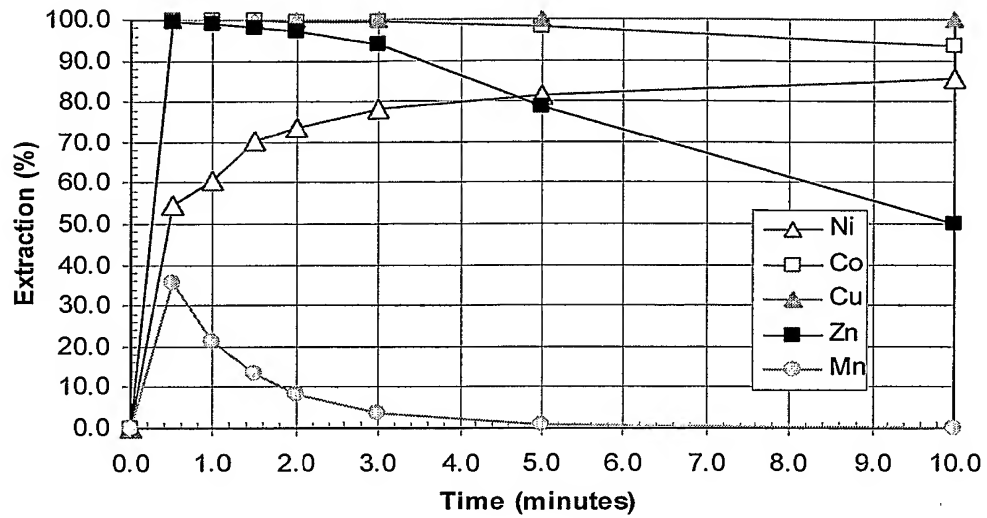


Figure 3

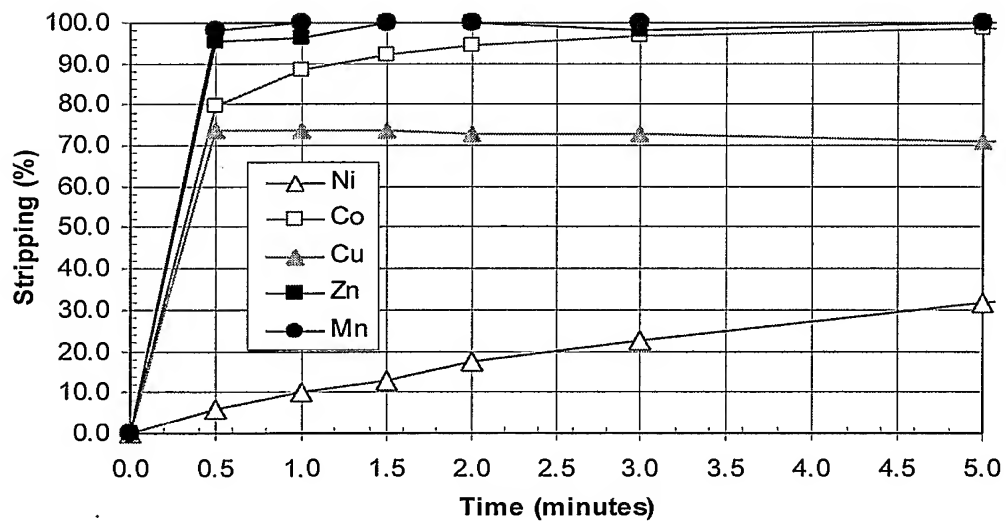


Figure 4

3/9

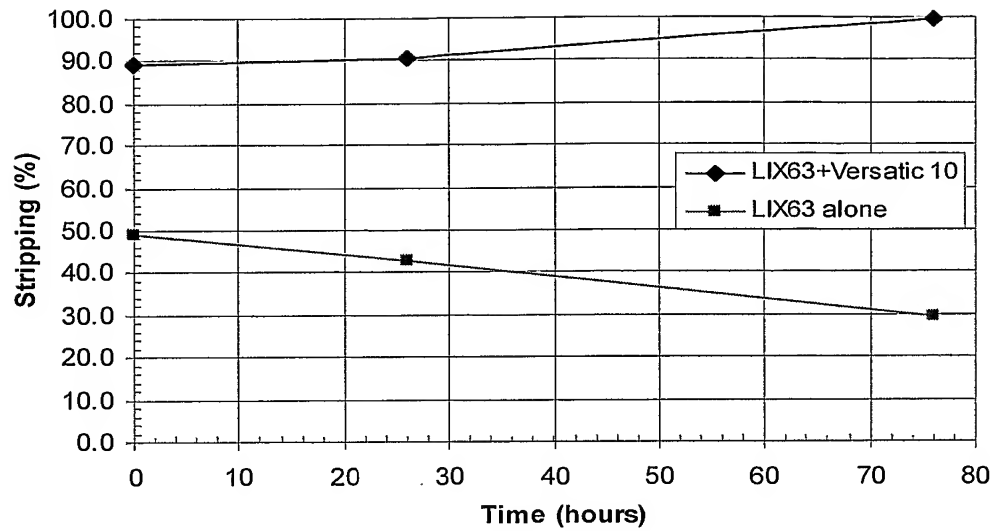


Figure 5

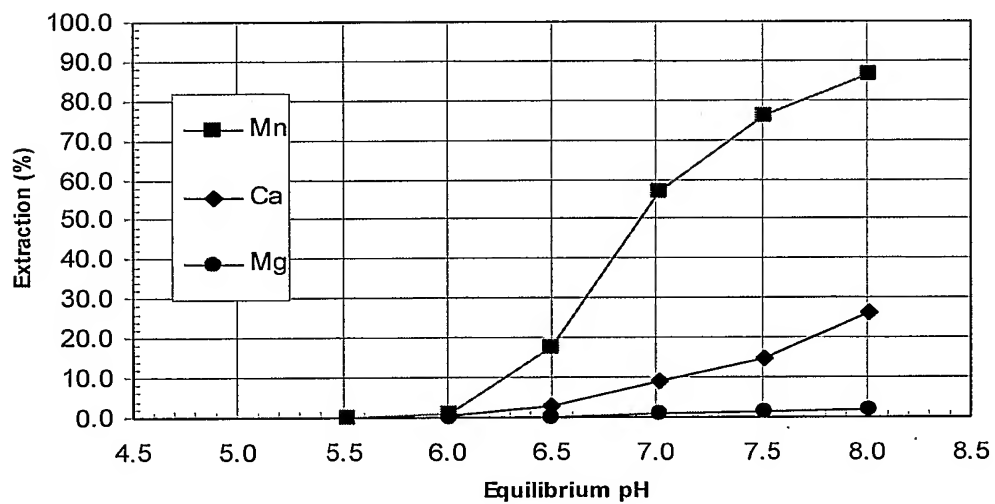


Figure 6

4/9

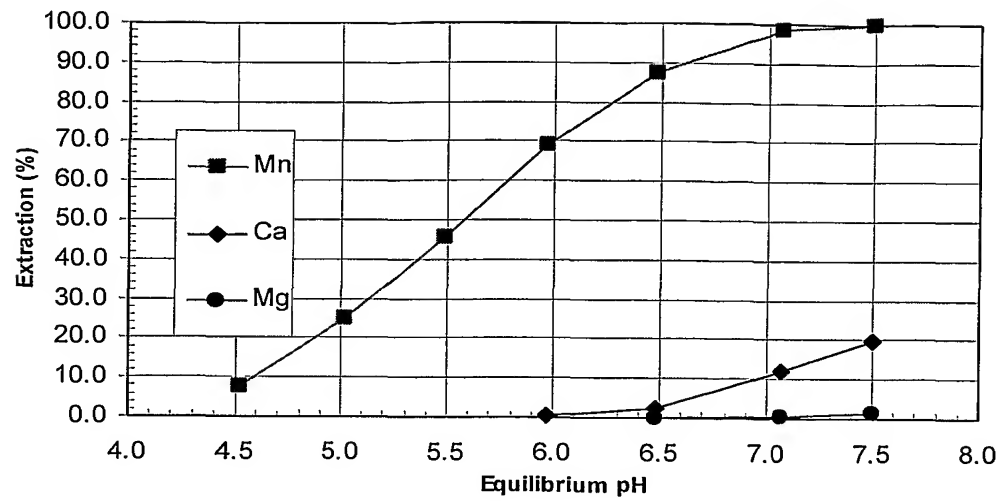


Figure 7

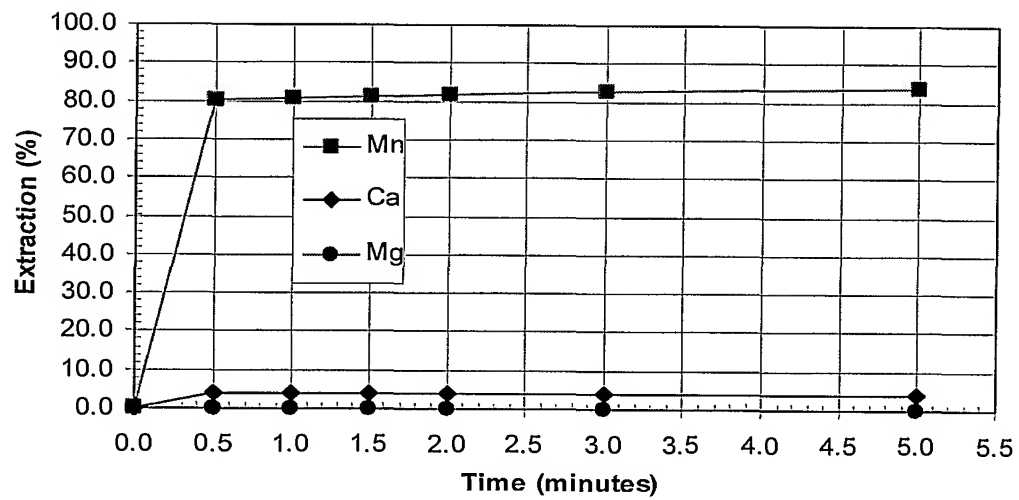


Figure 8

5/9

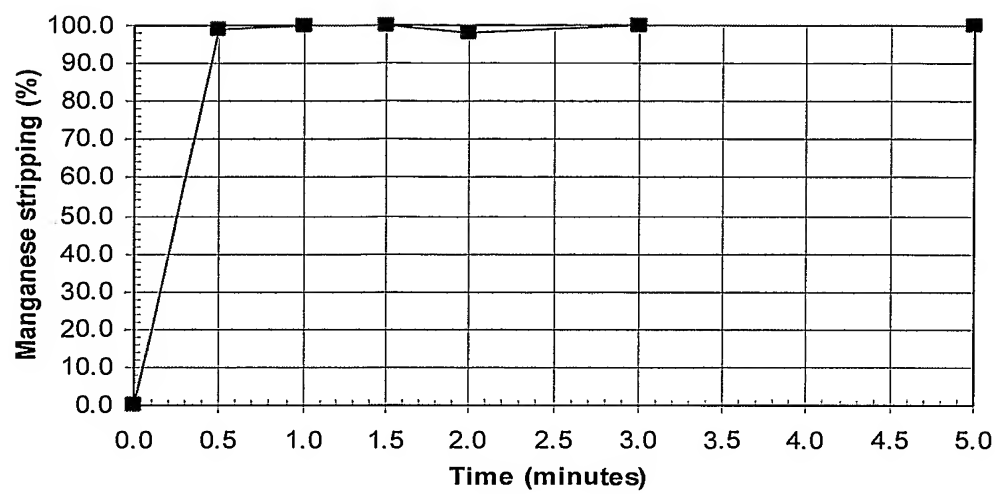


Figure 9

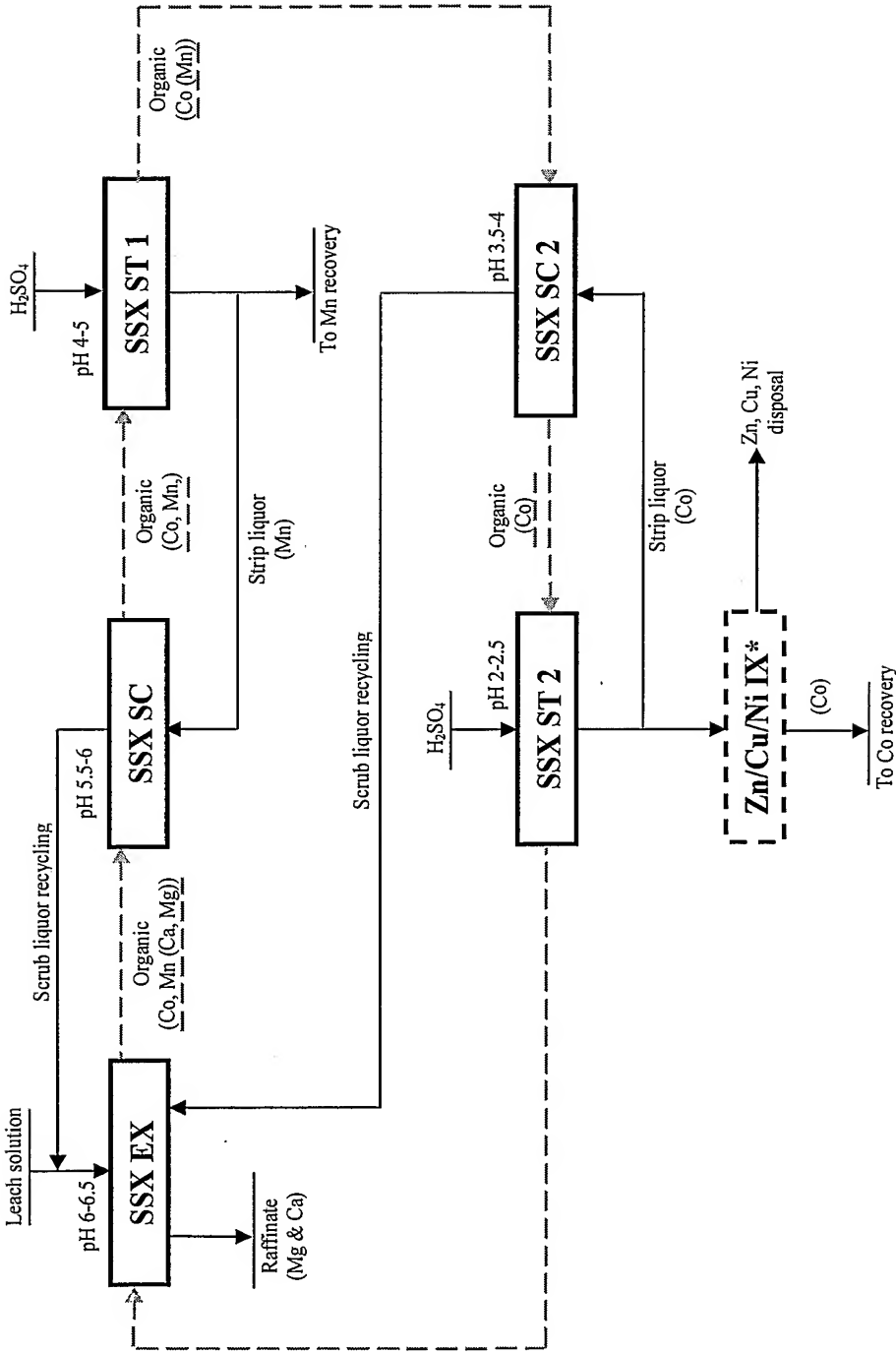


Figure 10

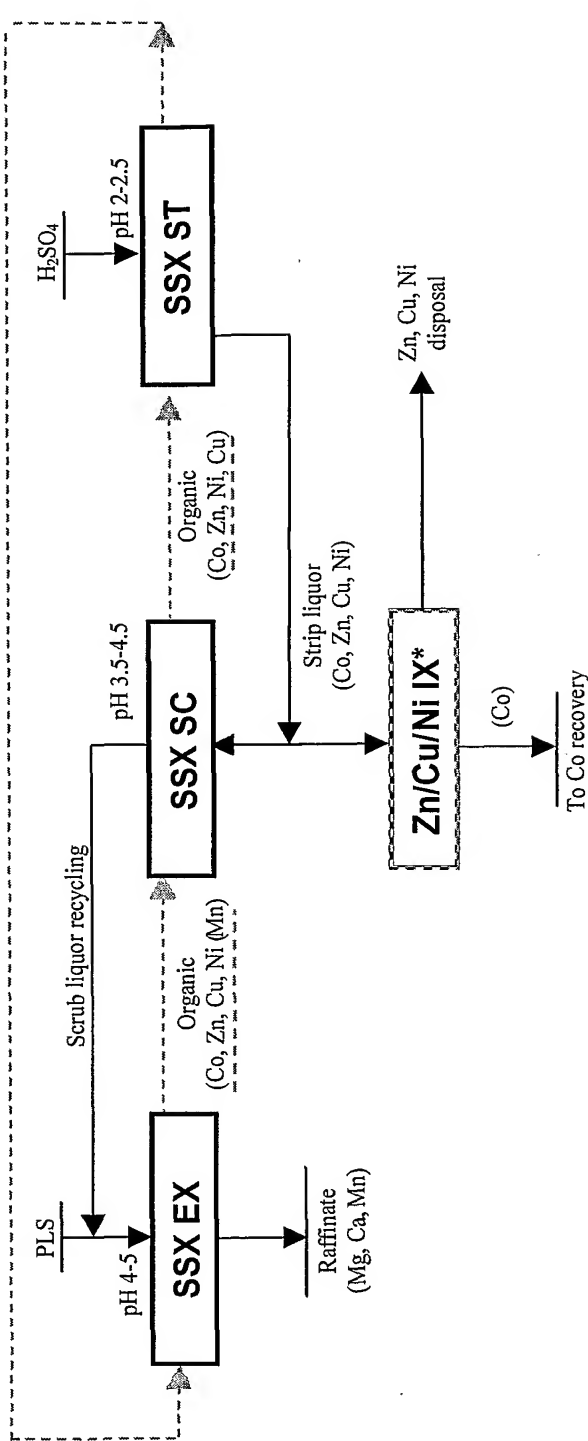


Figure 11



8/9

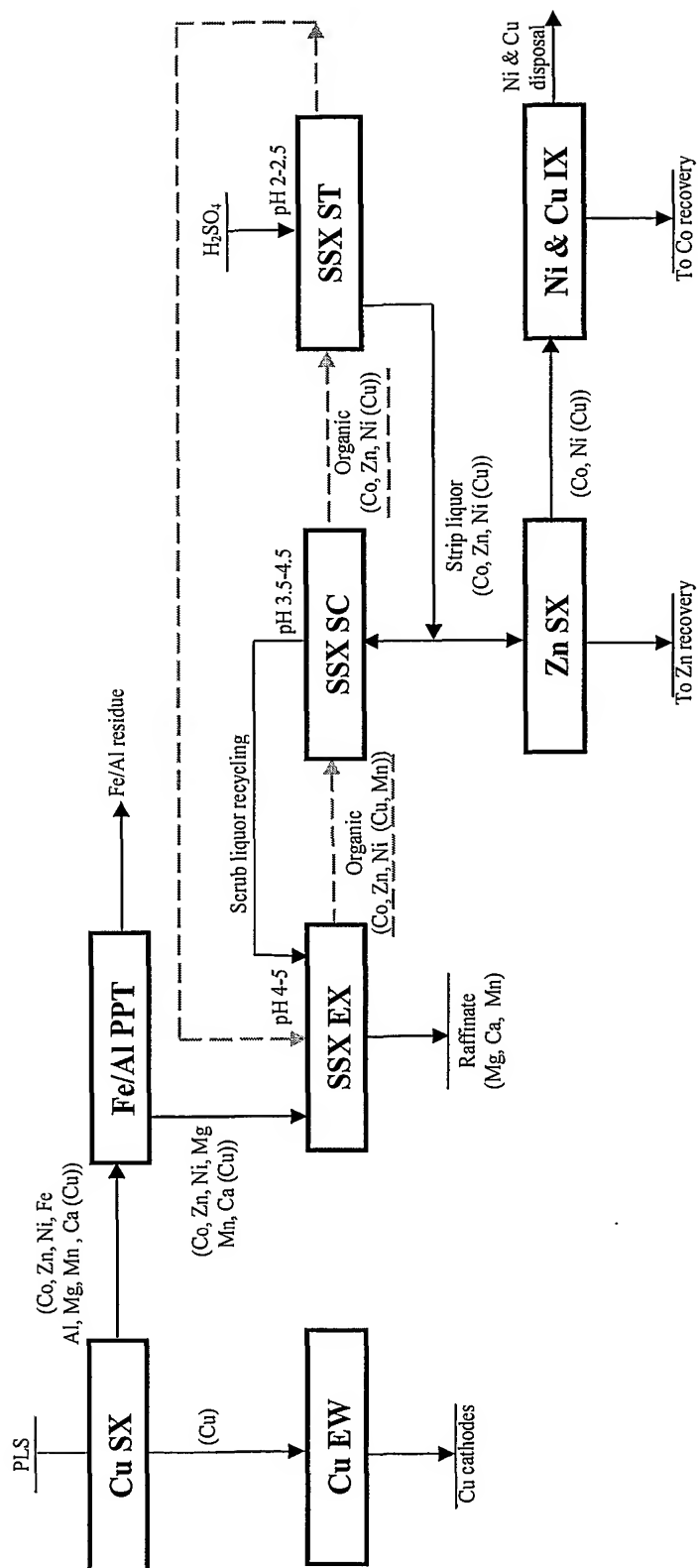


Figure 12

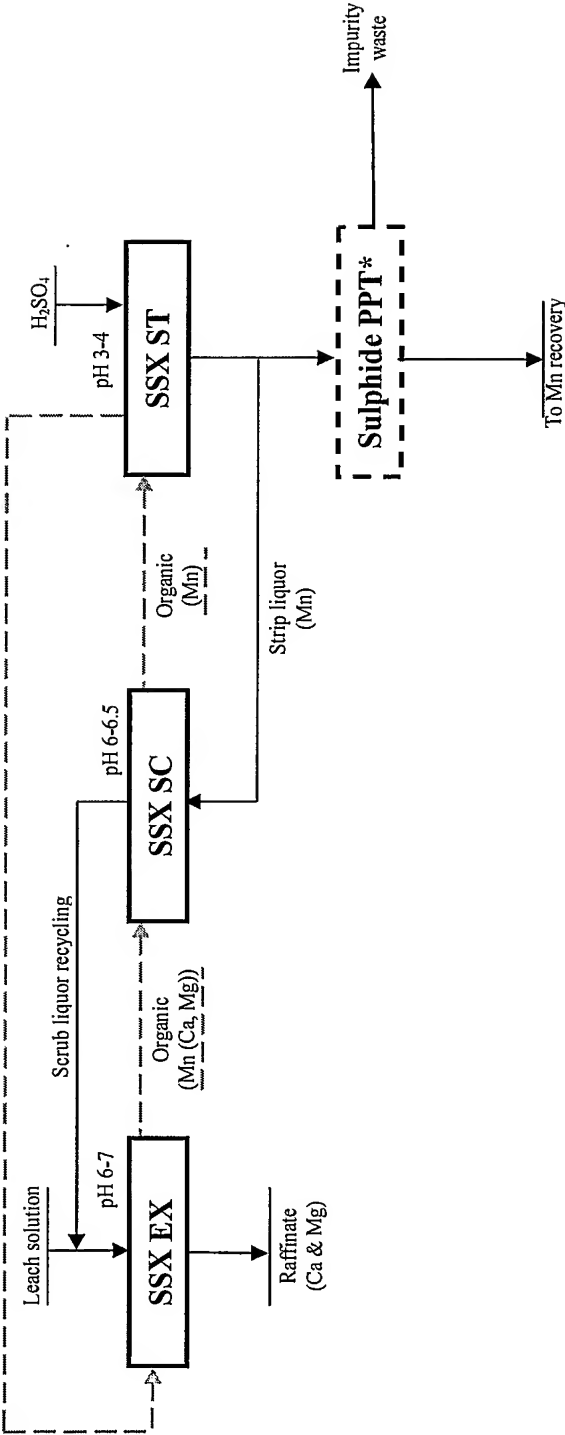


Figure 13

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/000088

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. <sup>7</sup>: C22B 3/40, 23/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup> C22B 3/40, 23/00, 3/30, 3/32 3/00, 15/00, 19/00, 47/00 ; IPC<sup>4</sup> C22B 23/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI IPC as above with key word +oxime+; C22b 19/00, 15/00 with key word hydroxyoxime

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No. 84-109393/18, Class E31, J01, M25, ES 8401143 A, (Schortmann P C), 16 February 1984 Abstract	1- 23
A	US 3903235 (Cardwell et al.), 2 September 1975 Whole Document	1- 23
A	GB 2109357 A (Council for Mineral Technology (South Africa)), 2 June 1983 Whole Document	1- 23
A	WO 1998/014623 (International Curator Resources Limited), 9 April 1998 Whole Document	1- 23

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 February 2005

Date of mailing of the international search report

24 FEBRUARY 2005 24 FEBRUARY 2005

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2005/000088

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA 1223242 A (Granted to Majesty (Her) in right of Canada as represented by the Minister of Energy, Mines and Resources, Canada), 23 June 1987 Whole Document	1- 23
A	WO 2002/022896 A1 (Commonwealth Scientific and Industrial Research Organisation), 21 March 2002 Whole Document	1- 23

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2005/000088

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
ES	8401143	PT	77614				
US	3903235	AU	57495/73	CA	951905	CA	951908
		CA	951909	CA	988713	CA	989180
		CA	991413	CA	1004472	CA	1005236
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		ZM	3582	ZW	9882		
WO	9814623	NIL					
CA	1223242	NIL					
WO	0222896	AU	93468/01	AU	93469/01	AU	93470/01
		CA	2421970	EP	1330555	US	2004050212
		WO	0222897	WO	0222898		
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							